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(54) **Process for preparing ionic exchange and adsorbent resins**

(57) A suspension polymerization process for the production of porous ion exchange or adsorbent resin is carried out at an excess pressure of 0.1-15 bar, which may be exerted due to the partial pressure of the ingredients or of an inert additional component such as an inert gas.

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Process for preparing ionic exchange and adsorbent resins

This invention relates to an improved preparation of macroporous ionic exchange resins, and adsorbent resins.

Advantages of macroporous ionic exchange resins are well known as compared to those which have a gel-structure. Some of these advantages are good kinetic characteristics, adsorbing ability of organics, good osmosis stability, excellent chemical and thermal characteristics.

These resins are widely used in practice.

Macroporous polymers are produced by suspension polymerization of vinyl monomers or monomers containing two or more vinyl groups using pore-forming agents. These additives developing porosity should be inert from the point of view of polymerization. After copolymerization the additives are removed by distillation, extraction or dissolution.

The obtained co-polymers are sulphonated if cation exchange resins are required and chloromethylation plus amination are applied if anion exchange resins are to be produced.

The main differences in the known processes can be found in the use of different pore-forming agents. The known processes can be classified as follows:

- a) Liquids are used as pore-forming agents, such as aliphatic, cyclo-aliphatic hydrocarbons and aliphatic, cyclo-aliphatic alcohols, these compounds act as solvents for vinyl monomers, or monomers having more than one vinyl groups but they swell polymers only slightly. If liquid pore-forming agents are applied the pore-forming agent and initiator for radical polymerization are dissolved in the vinyl monomer and polymerized at a proper temperature.

Removal of pore-forming agents from beads is completed mainly by steam distillation.

Mostly used pore-forming agents are: hexane, n-heptane, i-octane, benzene derivatives, petrol-ether, n-butyl alcohol, amyl alcohol, cyclohexanol, etc. These processes are described in British Patents Nos. 349 122, 942 328, 1 269 936; West-German Patent No. 1 045 102; French Patent No. 1 237 343, Japanese Patent No. 50-99 641, US Patent No. 3 343 563.

- b) If linear polymers [polystyrene, poly(ethylstyrene), poly(ethyl-methacrylate), poly(ethyl-acrylic-acid), nylon, aliphatic polyesters] are used as pore-forming agents then these polymers are dissolved in the starting vinyl monomer and after co-polymerization they are extracted with solvents (toluene, benzene, dichloro-ethane), or in certain cases they are saponified and dissolved.

These processes are described in British patents Nos. 1 082 635 and 1 115 019; Czechoslovakian Patent No. 169 290; Italian Patent 653 359; U.S. Patent No. 3 122 513; Hungarian Patent 142 661; French Patent No. 1 433 946.

- c) Solvents can be also applied with pore-forming agents. The presence of the proper quantity

of solvents is advantageous to the structure and porosity of the end product. Solvents used - among others - are aromatic and aliphatic hydrocarbons, chlorinated aliphatic and aromatic hydrocarbons (benzene, toluene, xylene, chloro-benzene, dichloro ethane), ketones, esters.

These methods of forming macroporous structure are described in British Patent Nos. 1 269 906 and 1 483 578; French Patent No. 2 044 630; Japanese Patent No. 53-32 867; West-German Patent No. 2 12 443.

Adsorbent resins are specific ionic exchange materials differing from macroporous ion exchange resins. The difference in the composition of adsorbent resins over ionic exchange resin is that they do not contain active groups, generally, their specific surface, or pore-volume is much higher than that of the ionic exchange resins. In the production of macro-porous ionic exchange matrices and adsorbent co-polymers inert materials are often used as pore-forming agents and such solvents as have a boiling point near to the temperature of polymerization, consequently their tension is relatively high at the temperature of polymerization. Ionic exchange matrices are prepared mostly in an aqueous medium by suspension polymerization. A non-mixing solvent system is used comprising an organic and a water phase. The boiling point of this system is lower than that of the components.

A disadvantage of this method is that the inert material, or a part thereof can escape from the suspended monomer mixture during reaction, and the obtained polymerizing beads have a semimacro, or gel like structure. It may also occur that due to the relatively high tension of the inert material, the diameter of the pores will be bigger than normal. The inert materials define the polymerization temperature, therefore from the point of view of quality of a co-polymer, an optimum profile of temperature cannot be attained.

Pore-forming agents and solvents are removed from the polymer after co-polymerization by distillation or extraction. The solvents and/or pore-forming agents can be retained by removing them from the beads by distillation, preferably by steam distillation. During polymerization problems may arise mainly because of the relatively low boiling point of the water phase organic phase system, the speed of evaporation of the pore-forming agents is too high even at relatively low temperatures and more pore-forming agent is removed from the suspended beads than required.

For the preparation of co-polymers suitable for adsorbents and ionic exchange resins having a proper porosity, specific area, suitable volume and mass capacity, it is necessary to keep the ratio of pore-forming agents and monomers within narrow limits. The porosity required cannot be attained during polymerization because the ratio

may change due to the alterations of the production step.

The following disadvantages should also be taken into consideration:

Since polymerization should be completed at a relatively low temperature, unreacted monomer remains in the end product. A postreaction occurs when pore-forming agents are distilled due to the high temperature. This fact has a negative effect on porosity. This disadvantage can be eliminated if an inhibitor is applied during removal of the pore-forming agents.

Care should be taken during polymerization about the proper heating of the reactor and the difference in temperature between temperature of polymerization and that of the reactor wall. If this difference is not small enough, the suspended monomer and ^{or} polymer beads are overheated at the wall of the reactor and thus pore-forming agent may escape. On the industrial scale due to the relatively low temperature difference permitted, the rate of heating is low, therefore a longer period is required to reach the temperature of polymerization.

Polymerization times are therefore rather long, due to the relatively low polymerization temperature. Using iso-octane, as pore-forming agent polymerization should be completed atmospherically under a temperature of 75 °C, where polymerization time is about 6-12 hours.

It is an object of this invention to eliminate the disadvantages in the preparation of macroporous ionic exchange and adsorbent resins using known methods.

Thus, according to the process of the present invention in the preparation of macro-porous ionic exchange resins by polymerization of vinyl monomers and of compounds having more than one vinyl group in the molecule in the presence of pore-forming agent and a catalyst, using suspension polymerization, and removing after polymerization the pore-forming agent and solvent with distillation or extraction the improvement consists of performing the polymerization - depending on the pore-forming agents applied - under an overpressure of 0,1-15 bar. This pressure can be attained also with a partial pressure of the components used and heated in a closed system. Preferably an inert gas, - such as N_2 gas - is applied; thus the boiling point of the system remains under the polymerization temperature used.

On realizing the instant process the reactor is flushed with nitrogen when all components required are added and the reactor is closed and put under the overpressure preferably by nitrogen. Overpressure - at the starting period of reactor's heating in case of iso-octane pore-forming agent - is about 2 bars and 6 bars when a pentane mixture is used.

The polymerization is completed between 50 and 120 °C, preferably between 70 and 97 °C. To form a proper polymer structure, polymerization time should be initially at temperatures between 70 and 90 °C 3-5 hours, and to reduce the remaining monomers a polymerization time of 2 hours is required at a temperature between 90 and 97 °C, with the use of two catalysts. In this case one of the catalyst acts at lower temperature, the other catalyst works at the temperature of post-polymerization.

The pore-forming agents are removed after polymerization by known methods. Such pore-forming agents are as follows:

- liquids, which can be removed by distillation or steam distillation;
- simultaneously pore-forming agents and solvents;
- simultaneously polymers, soluble in vinyl monomers solvents.

According to this invention, the components of polymerization may be as follows.

- Vinyl monomer compounds;

Ethylene-like monomers, containing unsaturated double bond and monomers with one vinyl group, such as vinyl monomer derivatives with aliphatic groups or halogen (styrene, vinyl-chlorobenzene, vinyl naphthalene, vinyl anisol, ethyl-vinyl benzene), aliphatic vinyl monomers and mono-vinylidene carboxylic acids and their

derivatives (methyl acrylate, ethyl acrylate, methyl methacrylate, methacrylic acid, ethyl acrylic acid, acrylonitrile, etc.). The preferred monomer is styrene.

- Crosslinking agents; compounds with two, or more ^{unsaturated} bonds (polyenes); aromatic compounds with more than one vinyl group, glycol diesters of aliphatic, unsaturated carboxylic acids, esters of aliphatic carboxylic acids with unsaturated alcohols (divinyl benzene, divinyl ethyl benzene, divinyl xylenes, divinyl toluene, divinyl naphthalene, 2,4,6-trivinyl ethyl benzene, ethylene glycol diacrylate, ethylene glycol dimethacrylate, diallyl adipate, diallyl maleate, diallyl fumarate, butadiene, isoprene, cyclo-pentadiene, diallyl phthalate, diallyl isophthalate, triallyl isocyanurate, diallyl succinate, diallyl carbonate, diallyl sebacate, diallyl tartarate, diallyl oxalate, triallyl citrate, N,N'-methylene diacryl amide).

- Pore-forming agents; aliphatic and cyclo-aliphatic hydrocarbons (such as butane, pentane, hexane, heptane, iso-octane, nonane, decane, cyclo-pentane, cyclo-hexane), aliphatic or cyclo-aliphatic alcohols (such as propyl alcohol, butyl alcohol, amyl alcohol, cyclohexanol), benzine and petroleum distillates, paraffinic oil; polymers soluble in vinyl monomer and monomer containing more than one vinyl group (such polystyrene, poly/methyl styrene/, poly/vinyl acetate/, poly/iso-

-butylene/, poly/methyl methacrylate/, poly/ethyl methacrylate/, poly/butyl methacrylic acid/, poly/vinyl xylene/, styrene, butadiene copolymer).

In addition to these compounds, pore-forming agents also can be used which are described in Italian Patent No. 653 359, Belgian Patent No. 856 502, British Patent No. 1 483 587, Japanese Patent No. 75 123 088.

- Solvents; aromatic and aliphatic hydrocarbons, chlorinated aliphatic and aromatic hydrocarbons (benzene, toluene, xylene, chlorobenzene, tetra-chloro-methane, tetra-chloro-ethane, dichloro ethane, ethyl benzene), ketones (methyl-isobutyl ketone), esters (n-butyl acetate, hexyl acetate).

- Stabilizers; mostly used stabilizers: poly(vinyl alcohol), sodium polymethacrylate, sodium polyacrylate, carboxy methyl cellulose, starch, poly(ethylene-glycol), dextrin, hydroxy ethyl cellulose, polyasacharides, poly(vinyl pyrrolidone).

- Catalysts; initiators used to radical polymerization, as dibenzoyl peroxide, terc-butyl peroxide, cumol peroxide, terc-butyl hydroperoxide, acetyl peroxide, terc-butyl perbenzoate, methyl-ethyl-ketone peroxide, azobis-iso-butironitrile.

Quantities and ratio of components are generally within the limits described below, calculated to the total mass of vinyl monomers and compounds containing more than one vinyl groups.

- vinyl monomers: 40-99 % by volume (preferably 75-95 % by volume)
- compounds with more than one vinyl group: 1-60 per cent by volume (preferably 5-25 % by volume)
- pore-forming agents: (depending on the pore-forming agents applied, volume of pores required, specific area), 5-150 % by volume,
- solvents: (depending on the type of solvent and structure of pores) 10-300 % by volume (preferably 15-130 % by volume),
- catalysts: 1-3 %, by mass,
- stabilizers: 0,05-5 % by volume, calculated on the polymerization medium.

The following examples illustrate the present invention:

Example 1

Medium of suspension polymerization was prepared so that 160 g of starch was boiled in 8000 cm³ of water as stabilizer. To the solution prepared and cooled, depending on the particle size required, 210 g of styrene, 65,6 g of divinyl benzene of 61 % by volume, and mixture of 165,4 g of iso-octane, 5,5 g of dibenzoyl peroxide, 2,7 g of terc-butyl perbenzoate were added with stirring.

Thereafter the reactor was flushed with nitrogen then closed. An over-pressure of 2 bars was adjusted with nitrogen. The polymerization was effected for 4 hours at 70-90 °C and 2 hours at 90-97 °C.

When the reaction was completed, temperature in the reactor was 95 °C and the overpressure 3,95 bars. Iso-octane was distilled by steam distillation.

(Yield 146 g.) The obtained polymer was filtrated, washed and dried. An opaque macroporous polymer was obtained 50 g of polymer, prepared as described, was swollen in dichloro-ethane, then 300 g sulphuric acid of 98 % by volume was added to a sulphonating flask and the polymer was sulphonated for 5 hours at a temperature between 80 and 105 °C.

After sulphonation the mixture was diluted with water. Four per cent by volume sodium carbonate solution was added to convert ionic exchange resin into Na^+ form. Next step was filtration. 220 ml³ of cationic exchange resin resulted had a highly acidic character. Data of resin are found in Table 1.

Example 2

Process of Example 1 was repeated with the difference that pentane was added instead of iso-octane and an overpressure of 7 bars was adjusted with nitrogen. Characteristics of product resulted are ^{to be} found in Table 1.

Example 3

Medium of suspension polymerization was prepared so that 160 g of starch was boiled in 8000 cm³ of water as stabilizer. 254 g of styrene, 26 g of 64 per cent by volume divinyl benzene, and mixture of 163 g of iso-octane, 5,6 g of dibenzoyl peroxide, 2,8 g of tert-butyl perbenzoate was added to the cooled polymerization medium.

Polymerization was completed as described in Example 1. 150 g of polymer was added to a flask, equipped with a stirrer, than 150 g of zinc chloride and 440 g of monochlorine methylether was put into the flask. Mixture was chloromethylated for 5 hours at 40-42 °C. Excess of monochlorine methylether was decomposed by methanol and neutralized by washing. Chloromethylated polymer was aminated with 740 ml of trimethyl amin of 40 % by volume for 5 hours at 35-40 °C. 1400 cm³ of highly basic anion exchange resin resulted. Characteristics of this resin are shown in Table 1.

Example 4

Process of Example 3 was repeated. The only difference was that 190 g of iso-octane was used. Characteristics of product resulted are shown in Table 1.

Table 1

Characteristics	1.	Examples 2.	3.	4.
Volume capacity (mekV/ccm)	1,65.	1,68	1,2	1,0
Mass capacity (mekV/g)	4,65	4,57	4,0	3,9
Change of volume (H^+/H^+ , per cent)	4,0	3,7	12,0	11,5
Volume of pores ml/g	0,26	0,35	0,025	0,031

Volume of pores was defined by CARLO-ERBA type porosimeter between 1 and 1000 bars with mercury penetration.

Example 5

Process was carried out as in Example 1. The difference was that 194 g of styrene, 81 g of divinyl benzene (61 % by volume), 192 g of n-heptane were added to the catalyst and overpressure with nitrogen was adjusted to 6 bars. Polymer resulted has a pore-capacity of $0,4184 \text{ cm}^3/\text{g}$, specific area is $90,6 \text{ m}^2/\text{g}$.

When processed according to Example 1, a highly acidic cationic exchange resin was obtained.

Example 6

Preparation of adsorbent resin. Polymerization was carried out as in Example 1 but 158 g of styrene, 117 g of divinyl benzene (61 % by volume), 275 g of iso-octane and 56 g of toluene were added to the catalyst.

The polymer resulted has a pore-volume of 0,6856 ml /g and a specific area of 286- m^2/g .

Example 7

Preparation of an adsorbent resin polymerization was completed as in Example 1 but 120 g of styrene, 160 g of divinyl benzene (61 % by volume), 28 g of polystyrene having a molecular weight of 5.2×10^3 , and 280 g toluene were added to the catalyst.

After co-polymerization, polystyrene is extracted by toluene.

Pore-volume of macroporous co-polymer resulted is 0,6528ml /g and specific area is 302 m^2/g by BET.

Example 8

160 g of starch was boiled in 8000 cm^3 water. Depending on the particle size of the resin to be prepared a mixture of 18 g of divinyl benzene (61 % by volume), 14 g of acrylnitrile, 28 g of methyl acrylate, 220 g of ethyl acrylate were added as monomers to the prepared and cooled polymerization medium while stirring. Then a mixture of 5,5 g of di-

benzoyl peroxide and 2,7 g of terc-butyl perbenzoate was dissolved in 170 g of iso-octane and the mixture was also added.

The equipment was flushed with nitrogen and put under an overpressure of 2,5 bars. The mixture was polymerized for 5 hours at 75-90 °C and for 2 hours at 90-97 °C.

Then iso-octane was distilled off by steam distillation. Opaque beads resulted were washed and dried. Their weight was 268 g. Quantity of iso-octane reclaimed was 142 g. 50 g of polymer, prepared as described, was added to a suphonating flask with aqueous potassium hydroxide of 20 % by volume and the mixture was hydrolysed for 6-8 hours at 75-100 °C, then diluted with water and formed to H⁺ form with hydrogen chloride of (8-10 % by volume) and filtrated.

132 cm³ of slightly acidic cationic exchange resin resulted had a pore volume of 0,09 ml³/g and a mass capacity of 9,3 meq/g.

Example 9

To prepare a selective ion exchange resin 100 g of chloromethylated and neutralized polymer of Example 3 was reacted with 100 g of thio-urea in 1000 ml of water. The mixture was stirred for 3 hours at 82-86 °C. Nitrogen content of product was 11,5 per cent by volume. This ionic exchange resin is capable to adsorb Au, Ag, Pt, Pd and Hg.

Example 10

Medium of suspension polymerization was prepared so that 160 g of starch was boiled as stabilizer in 8500 ml of water. Medium of polymerization was then cooled and 213 g styrene, 62 g divinyl benzene (61 % by volume) and 5,5 g dibenzoyl peroxide in 206 g iso-octane were added. The equipment was flushed with nitrogen and closed. The process was carried out similar to Example 1 but without nitrogen over-pressure. Polymerization was carried out between 70 and 95 °C. The pressure increased, during polymerization up to 1,35 bar. 250 g polymer resulted was sulphonated as in Example 1 and a highly acidic, macroporous ionic exchange resin was obtained.

Mass-capacity: 4,3 meq/g.

Change in volume Na^+/H^+ : 3,2 %.

Pore-volume of polymer: 0,18 ml /g.

Example 11 (comparative)

Process was carried out as in Example 1 but polymerization was completed without pressure. The polymer obtained had a gel structure, pore-volume was 0,0154 ml/g, the specific surface could not be determined by BET.

Example 12

Polymerization process was repeated as in Example 1 but 140 g of styrene, 135 g of divinyl benzene (61 % by volume), 320 g of isooctane and 82 g of toluene were reacted.

Pore-volume of polymer was 1,5169 ml/g and the specific surface 412 ml/g.

CLAIMS:

1. Process for the production of ion exchange resin or adsorbent resin by suspension polymerization of vinyl monomere and compounds containing more than one vinyl groups in the presence of pore-forming agent and catalyst, wherein the polymerization is completed in a closed system under excess pressure of 0.1-15 bar.
2. A process according to Claim 1 wherein solvent of the suspension and the pore-forming agent are removed by distillation or extraction, thereafter the polymer is converted to an ion exchange resin.
3. Processes according to Claim 1 or Claim 2 substantially as herein exemplified in Examples 1-10 and 12.